

Applying Thermo-Reactive Diffusion Method to Surface Coating of H13 Tool Steel Using Ferrovanadium, Ferrochromium, and Misch Metal

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Abstract

The thermo-reactive diffusion (TRD) process is a method for surface hardening that improves the hardness, corrosion resistance, and wear resistance of the materials. In this study, the effect of composition was investigated, by using 8, 12, 16, 20, and 24 wt% of ferrochrome and ferrovanadium with equal amounts, along with 3 wt% aluminum and borax. The TRD process was carried out at 1000°C for 7 hours on AISI H13 hot work tool steel so that a complex coating of chromium-vanadium carbide was formed on the H13 substrate. Optical and scanning electron microscopes were used to evaluate the thickness and microstructure of the samples, respectively. Moreover, the amount of alloying elements and constituent phases on the surface were analyzed by point analysis and X-ray diffraction. The micro-hardness method was used to evaluate the hardness of the samples. The results of this study showed that by increasing the amount of ferroalloy, the hardness and thickness of the coating increase. The optimal composition with 8% ferrochrome and 8% ferrovanadium was found to yield a coating with a thickness of 7.65 μm and a hardness of 2115 HV.

Keywords: thermo-reactive diffusion, H13, hot work tool steel, chromium-vanadium carbide

1. Introduction

Die degradation is one of the most undesirable and costly phenomena in forging industries. This phenomenon results from high temperatures, high forming pressures, impacts, and surface scaling. One of the best ways to increase the service life of dies is to use suitable coatings that can withstand these harsh working conditions. Chemical vapor deposition (CVD) and physical vapor deposition (PVD), which require complex and expensive equipment, are two widely used methods to produce such coatings. Low penetration, adhesion strength, and coating thickness are the limitations of these methods (Fritz & Russ, 2004; Babu, Ribeiro, & Shivpuri, 1999; Oliveira, Benassi, & Casteletti, 2006; Azizi & Soltanieh, 2014; Wei & Chen, 2005; Babu, 2004; Fazl & Aghaei, 2009). Thermo-reactive diffusion (TRD) is one of the coating processes for solving the mentioned problems (Babu, Ribeiro, & Shivpuri, 1999). In this method, a layer consisting of vanadium, titanium, chromium, and/or niobium carbide is deposited on steels with at least 0.3% carbon in a cost-effective manner and without the need for complex equipment (Oliveira, Benassi, & Casteletti, 2006; Azizi & Soltanieh, 2014; Wei & Chen, 2005; Babu, 2004). According to the literature, the service life in this method increases up to 10 times (Fazl & Aghaei, 2009). Temperature, time, and composition of the salt bath are among the parameters that affect this process. The temperature can be varied from 800 to 1200 °C and the time from 1 to 10 hours. Under these conditions, with increasing temperature and time, the thickness of the layer increases (Shirinbayan, Shafyei, & Aboutalebi, 2014; Sen, 2005; Arai et al., 1987; Sen, 2005).

In the present study, first, the percentages of ferroalloys and the optimal composition of vanadium-chromium carbide coating on H13 steel were determined to achieve the highest hardness and thickness. Then, a facilitator (misch metal (Liu et al., 2021)) was added to the optimal salt bath, and the coating acceleration was examined for reducing the process time.

2. Materials and Method

In this research, H13 hot work tool steel with the chemical composition given in Table 1 was used. The steel specimens were prepared in the form of tablets with a diameter of 3.5 cm and a thickness of 1 cm. Then, a 3-mm diameter hole was made in the specimens to hang and immerse them in a salt bath. All specimens were ground by 60 grit sandpaper before heat treatment and then ultrasonically cleaned for 20 minutes. The salt bath was composed of industrial borax with the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$, ferrovanadium powder, ferrochromium powder, and aluminum powder as an oxygen reducing agent. The specimens were subjected to 1000 °C over 7 hours of TRD process. The compositions of the used salt baths are given in Table 2.

Table 1. Chemical composition of H13 steel obtained using quantitative analysis

Element	C	Cr	Mn	Mo	P	S	Si	V	Fe
Weight percentage	0.39	5.2	0.3	1.5	0.015	0.005	0.96	1.1	Balance

Table 2. Different combinations of salt baths in wt% for 7 tested models

Sample name		Cr14	V14	Cr5 V5	Cr7 V7	Cr9 V9	Cr11 V11	Cr13 V13
Salt bath components	Borax	82	82	86	82	78	74	70
	Ferro vanadium	0	14	5	7	9	11	13
	Ferro chrome	14	0	5	7	9	11	13
	Aluminum	4	4	4	4	4	4	4

The heat treatment cycle of the samples is shown in Figure 1.

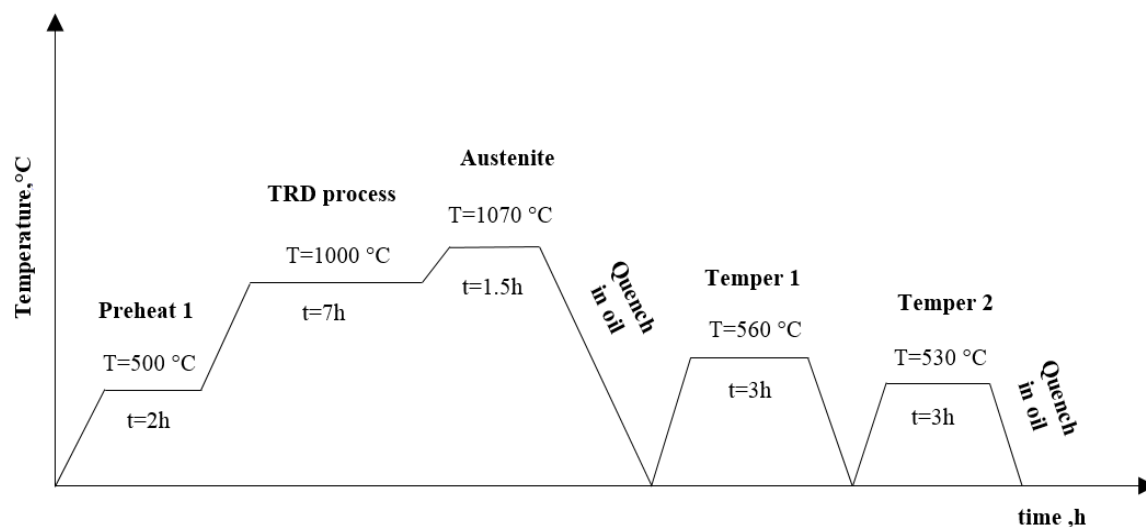


Figure 1. Heat treatment cycle and related parameters

In the next section, to accelerate the formation of the coating, a misch metal catalyst with the chemical formula FeSiRe_{23} (Table 3) was added to the optimal composition obtained in the previous section. This procedure was carried out at the same temperature but for 1 to 4 hours. The composition of these baths is shown in Table 4.

XRD analysis was carried out to determine the phase analysis using the X'Pert HighScore Plus.

Table 3. Chemical composition of FeSiRe23

Re	Ca	Si	Mn	Ti	Fe
22	4	46	2	2	Balance

Table 4. Composition of salt bath containing FeSiRe23 in wt%

Number of bath	FeSiRe23	Borax	Ferro chrome-Ferro vanadium	Aluminium
1	5	73	9-9	4
2	7	71	9-9	4

3. Results and Discussion

3.1 Microstructure Analysis

Figure 2 shows the formed coating of ferroalloys with different percentages. At the beginning of the TRD process, vanadium and chromium diffuse into the substrate to form a solid solution; when an equilibrium concentration is reached, the carbides begin to form. The thin layer of carbide on the surface prevents the diffusion of more carbide into the substrate (Fan et al., 2010a). For high percentages of ferroalloys, due to the high concentration of salt bath as well as high carbon activity in H13 steel, carbides are formed at the grain boundaries simultaneously with the formation in the coating. Figure 3 shows the optical microscope images of 16% Cr and 16% V samples. Vanadium carbide coating is more compact and uniform than chromium carbide.

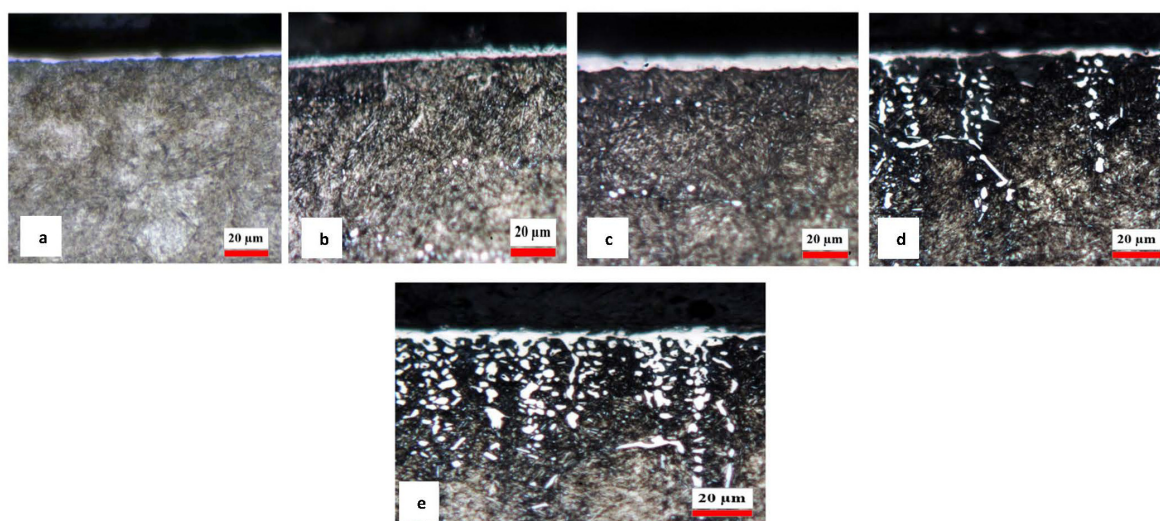


Figure 2. Optical microscope images of samples in salt baths; a) 4%Cr-4%V, b) 6%Cr-6%V, c) 8%Cr-8%V, d) 10%Cr-10%V, and e) 12%Cr-12%V at 1000°C for 6 hours

The non-uniformity and non-compactness of chromium carbide can be attributed to its high solubility at austenite temperature, which allows the diffusion of carbide from the coating to the substrate (Fan et al., 2010a). Figure 4 shows that the higher concentration of ferrochrome and ferrovanadium in Cr12V12 leads to a higher hardness compared to Cr4V4.

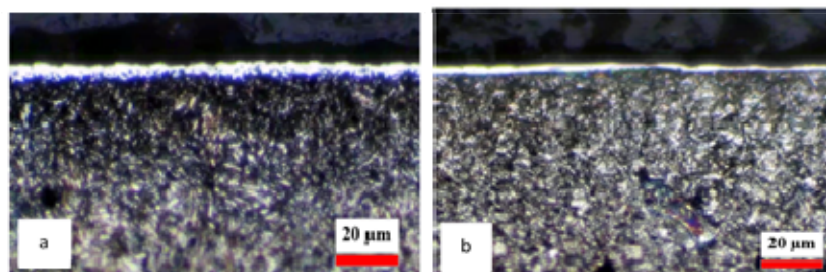


Figure 3. Optical microscope images of coating samples in salt baths: a) 16%Cr and b) 16%V at 1000 °C for 6 hours

Up to composition Cr8V8, the formed layer is still smooth and uniform. However, for higher concentrations of ferroalloy, the layer becomes non-uniform and there is no significant increase in hardness, which can be attributed to the insufficient carbon on the surface relative the amount of ferroalloys as well as the declining fluidity of the bath (Fan et al., 2010b; Orjuela-Guerrero, Alfonso-Orjuela, & Olaya-Flórez, 2015; S. Sen, U. Sen, & Bindal, 2005; Aghaie-Khafri & Fazlalipour, 2008). The sample Cr8V8 is optimal in terms of hardness and thickness because it yields a uniform coating and optimal hardness. Moreover, in this sample, carbides are not found in the substrate grain boundaries. Figure 5 shows the SEM image of the optimal composition (Cr8V8). As can be seen in this figure, the coating is uniform and compact while the coating-substrate interface is distinct and very little carbide is observed in the sub-layer. Table 5 shows the weight and atomic percentage of the surface and sub-surface elements of the optimal sample, which have been measured by quantitative analysis. The atomic percentage of surface carbon is higher than that of the substrate due to carbide formation. Figure 6 shows the phases formed on the sample with optimal coating composition (Cr8V8). Carbides V6C5 and Cr7C3 determine the hardness of the coating (Biesuz & Sglavo, 2009; Liu, Wang, & Li, 2008). Vanadium and chromium carbides form an FCC crystal lattice at 1000 °C with carbon atoms in the middle of the surface between vanadium and chromium atoms (Orjuela-Guerrero, Alfonso-Orjuela, & Olaya-Flórez, 2015).

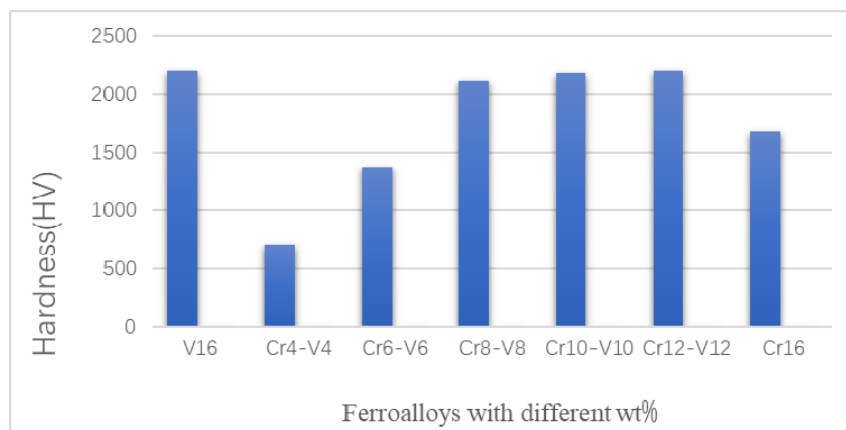


Figure 4. Hardness versus different percentages of ferroalloys at 1000 °C for 6 hours

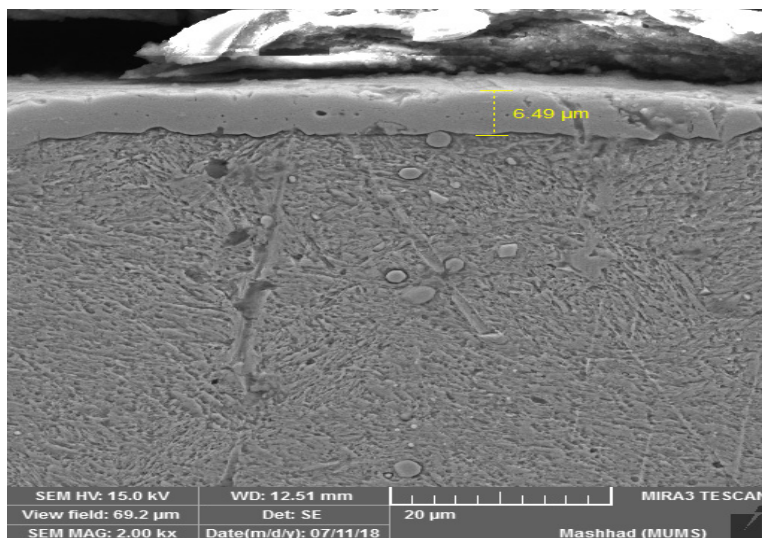


Figure 5. SEM of the optimal composition at 1000 °C for 6 hours

Table 5. Quantitative analysis of a) surface and b) sub-surface of coating with optimal composition at 1000°C for 6 hours

a)

Element	Wt%	At%
C	26.98	62.68
V	4.27	2.34
Cr	17.16	9.21
Fe	51.58	25.77

b)

Element	Wt%	At%
C	24.91	60.53
V	0.74	0.42
Cr	4.73	2.66
Fe	69.63	36.39

On the surface of the coating, there was also iron carbide. However, no solid solution peaks such as iron-chromium and iron-vanadium were observed in the coating. Additionally, stable phases of VC and Cr₃C₂ were not observed due to the insufficient surface carbon relative to vanadium and chromium.

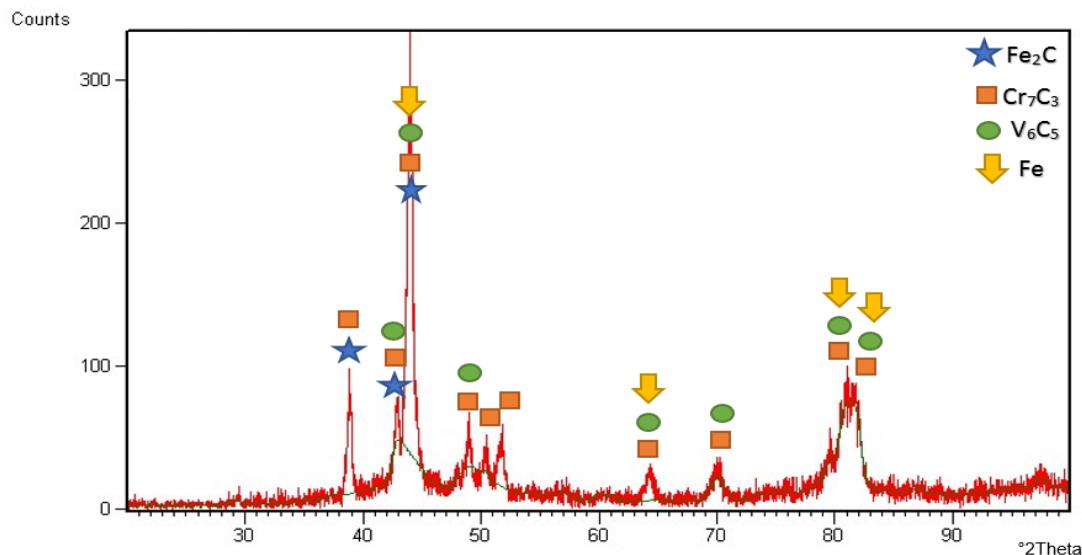


Figure 6. XRD of optimal coating composition at 1000 °C for 6 hours

In the next step, 3 wt% misch metal was added to the Cr8V8 salt bath to accelerate the formation of the coating.

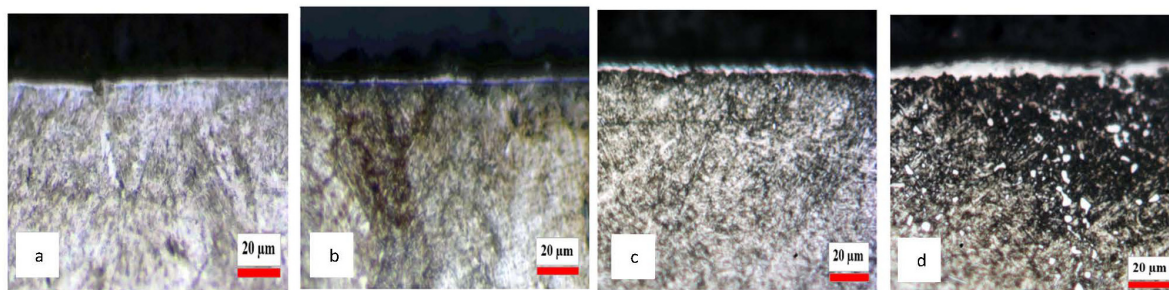


Figure 7. Optical microscope images after adding 3 wt% misch metal for a) 1, b) 2, c) 3, and d) 4 hours of immersion in the optimal salt bath at 1000 °C

For immersion times from 1 to 4 hours at a temperature of 1000 °C, the coating formation, hardness, and thickness of the layer were investigated and compared with the previous step. Figure 7 shows the optical microscope images of samples coated by adding 3 wt% misch metal to the salt bath. The addition of 4 wt% misch metal to the optimal bath for the same duration and temperature leads to the same results. Figure 8 shows the optical microscope images of 4 wt% misch metal for different time intervals. Similar to previous samples, the thickness of the coating layer increased with increasing time, and in 4 hours, a large amount of carbide was observed in the sub-layer. The layer was non-uniformly formed in 4 hours compared to the optimal bath (Cr8V8) without misch metal. Therefore, no more misch metal was added to the salt bath to compare with the optimal composition because the purpose of adding misch metal was to achieve the highest hardness and thickness in less time.

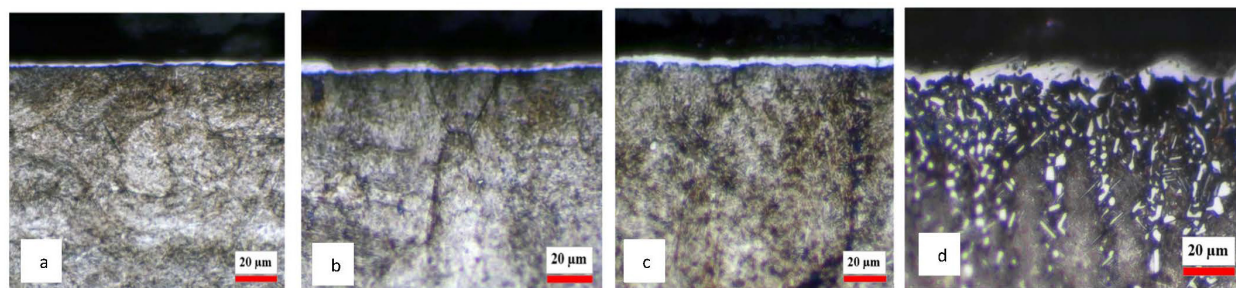


Figure 8. Optical microscope images after adding 4 wt% misch metal for a) 1, b) 2, c) 3, and d) 4 hours of immersion in the optimal salt bath at 1000 °C

Tables 6 and 7 show the hardness of samples coated in salt baths containing 3 and 4 wt% misch metal for different immersion times.

Table 6. Hardness of 3 wt% FeSiRe23 samples for different immersion times at 1000 °C

Sample name	Time(h)	Hardness (Hv)
Cr8V8+3%M	1	860
Cr8V8+3%M	2	1000
Cr8V8+3%M	3	1450
Cr8V8+3%M	4	1710

Table 7. Hardness of 4 wt% FeSiRe23 samples for different times at 1000 °C

Sample name	Time(h)	Hardness (Hv)
Cr8V8+4%M	1	1100
Cr8V8+4%M	2	1390
Cr8V8+4%M	3	1620
Cr8V8+4%M	4	1948

Figure 9 shows the SEM image of the sample coated for an immersion time of 4 hours in the optimal composition bath containing 4 wt% misch metal. The thickness of the layer has increased compared to the optimal composition, but a large amount of carbide is observed in the sub-layer. At the beginning of the TRD process, vanadium, chromium, lanthanum, and cerium diffuse into the substrate to form a solid solution, and when they reach an equilibrium concentration, carbides begin to form on the surface. When a thin layer is formed, it prevents the more diffusion into the sub-layer. However, for this amount of ferroalloy, the bath concentration is high and the misch metal has an accelerating effect on the decomposition of the solution and the adsorption of vanadium and chromium atoms. During long immersion in the salt bath, the carbon of H13 steel can react with chromium and vanadium, leading to nucleation and growth of carbides at grain boundaries.

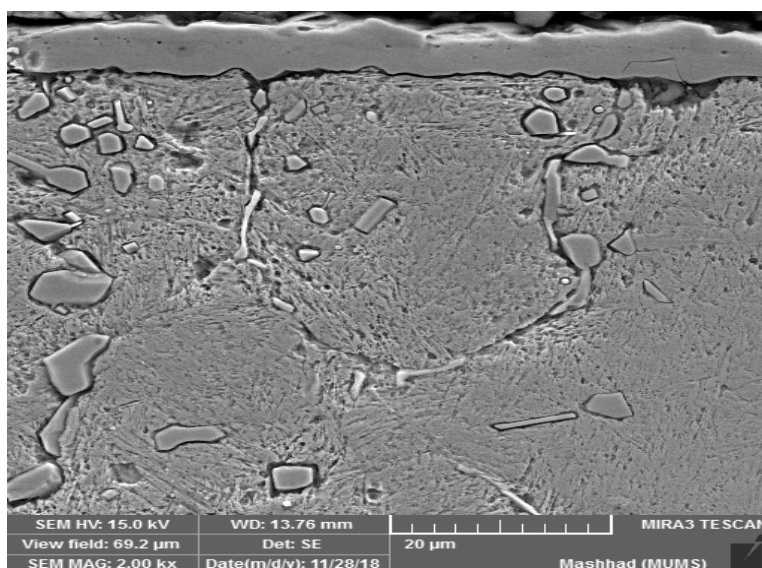


Figure 9. SEM of 4 wt% misch metal in optimal composition for 4 hours of immersion at 1000 °C

Figure 10 shows the phases existing on the surface of the Cr8V8 sample coated for 4 hours in the bath containing 4 wt% misch metal. In the sample containing misch metal, as in the previous step, chromium carbide of type M_7C_3 was found. The maximum peak intensity is between 40° and 50° . However, the type of vanadium carbide was different from that in the Cr8V8 sample. Misch metal increases the diffusion of vanadium and carbon. According to Fig. 10, the peak intensity of vanadium decreases with the presence of misch metal. It seems that this behavior is due to the lower amount of misch metal compared to carbide elements. Furthermore, the cerium and lanthanum peaks appear in the XRD pattern. Therefore, the misch metal cannot absorb the whole vanadium atoms and the hardness of this sample decreases compared to the optimal sample. In this sample, a new phase of vanadium-chromium carbide $(V_{46}Cr_{54})(V_{22}Cr_{78})_2C_{1.44}$ was also detected.

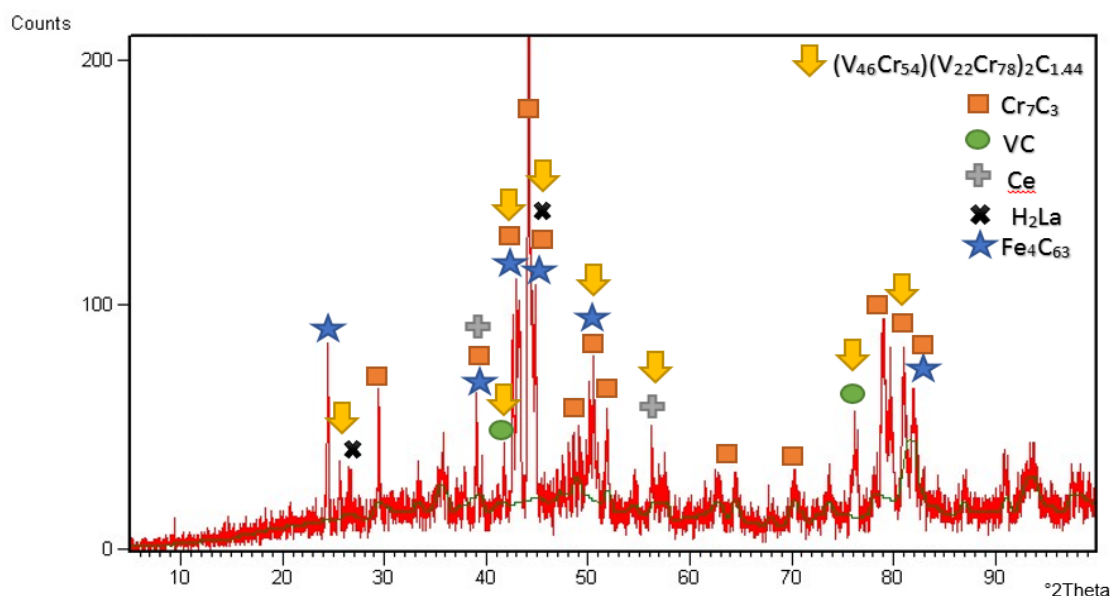


Figure 10. XRD of coating with 4 wt% misch metal in optimal composition for 4 hours at 1000 °C

4. Conclusion

Initially, the optimal composition in terms of hardness and thickness was selected from different percentages (from 8 to 20%) of ferrochrome and ferrovanadium with equal amounts. All of the samples were coated using the TRD method at 1000 °C for 6 hours.

As the amount of ferroalloy increased, the hardness and thickness of the coatings increased. However, beyond the Cr8V8 sample, the coating thickness was non-uniform and surface hardness did not significantly increase. In addition, grain boundary carbides, which result in the brittleness of the samples, were observed. Therefore, the Cr8V8 sample was selected as the optimal sample yielding a thickness of 7.65 μm and a hardness of 2115 HV.

With increasing time, the hardness and thickness increased in 3 and 4 wt% misch metal samples. However, for 4 hours of immersion, non-uniform thickness with carbides in the sub-layer was observed. In the presence of 4 wt% misch metal for 4 hours of immersion, the hardness was reduced compared to the optimal composition sample. The peak intensity of the VC phase in the sample containing misch metal is much lower than that in the optimal composition sample. That is why the hardness of this sample has decreased compared to the optimal composition.

Although the presence of misch metal improves the solubility of the salt bath and the adsorption of vanadium and chromium atoms, it reduces the hardness due to lack of carbon on the surface and the formation of undesirable carbides at the grain boundaries in a long time (4 hours).

Conflict of Interests

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report. We certify that the submission is original work and is not under review at any other publication.

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